MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

HgCdTe AVALANCHE PHOTODIODE DEVELOPMENT

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Group 85

FINAL REPORT

For Period 1 August 1978 to 30 September 1979

LEXINGTON   MASSACHUSETTS

ABSTRACT

The most significant achievement of the research program was our discovery that good quality $Hg_{1-x}Cd_xTe$ single crystal epitaxial layers could be grown on CdTe substrates by liquid phase epitaxy from Te-rich HgCdTe solutions over the entire range of x from 0 to 1.0. This was accomplished using an open-tube horizontal slider technique particularly adapted for solutions containing volatile mercury. Stimulated photoluminescence[1], optical transmission, electron microprobe, optical microscopy, x-ray diffraction, Hall coefficient and electrical resistivity measurements were carried out on various LPE-grown layers. These characterization techniques demonstrated that high quality HgCdTe epitaxial layers were prepared by our method.

The 425, 450, 475, 500, 525 and 550°C liquidus isotherms of the $Hg_{1-x}Cd_xTe$ primary phase field of the Hg-Cd-Te ternary phase diagram have been determined for the tellurium-rich corner of that system by a differential thermal analysis technique. These isotherms were used to help establish the conditions for the open-tube liquid-phase-epitaxial growth of $Hg_{1-x}Cd_xTe$ layers on $CdTe_{1-y}Se_y$ substrates, from the ternary liquid. Layers with x ranging from 1.0 to less than 0.2 have been grown with a horizontal slider technique particularly adapted for solutions containing volatile mercury. The electron beam microprobe technique was employed for the determination of the cadmium content of the epitaxial layers and the resulting data, along with the liquidus isotherms, were used to determine the liquidus-solidus isotherms. The layers are grown from a Te-rich HgCdTe solution in a H_2 flow and with less than 1 atm partial pressure of Hg over the melt. Growth temperatures and times in the 450-550°C and 15 sec to 10 min range, respectively, have been used. The melt equilibrium time is

typically 1 h at 550°C. A precursor wafer, supercooled solutions, and (111) oriented substrates are employed for growth of the highest quality layers, which are between 3 and 15 μm in thickness. The number of degrees of supercooling is typically 10 and 25°C for the (111)A and (111)B orientations, respectively. In addition to EMP data, various optical and electrical characterization results are given.

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I. INTRODUCTION

$Hg_{1-x}Cd_xTe$ has a number of interesting physical properties as well as numerous potential device applications. The II-VI pseudobinary alloys can be tailored to cover a broad range of energy gaps and temperatures and their basic properties such as high electron mobility, high mobility ratio, relatively low dielectric constant, long minority carrier lifetimes and high electrooptic coefficients are very suitable for the development of complex devices. Among the well-developed semiconductor alloy systems, HgCdTe is unique because device grade material can be prepared with both high energy band gaps (of interest for avalanche photodiodes and solar cells operating in the vicinity of 1 μm) and low energy band gaps (of interest for very long wavelength detectors and lasers operating in the vicinity of 10 μm and beyond). Although the lattice mismatch between HgTe and CdTe is only 0.3%, HgCdTe can be precisely lattice-matched to CdTeSe substrates[1]. Furthermore, there is a good thermal expansion coefficient match between the substrate and the alloy.

For the most highly developed semiconductor materials, such as Si and GaAs, epitaxial techniques have enabled the development of very high performance semiconductor devices. There is every reason to believe that the highest quality HgCdTe device structures will evolve from epitaxial rather than bulk material. However, at the present time, a developed technique for the preparation of high-quality epitaxially grown layers of HgCdTe does not exist.

Several possible methods for the growth of epitaxial layers have been investigated in the past. A close-spaced isothermal epitaxial film method for HgCdTe has been investigated[2,3]. Cathodic sputtering of HgCdTe films on

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single-crystal substrates of NaCl, Ge, and sapphire has been reported[4]. The formation of layers by Hg-ion bombardment of CdTe has been carried out, but an epitaxial growth layer was not achieved[5]. Polycrystalline layers of $Hg_{0.9}Cd_{0.1}Te$ were obtained by a simple thermal evaporation method[6]. The vacuum deposition of $Hg_{0.8}Cd_{0.2}Te$ was studied[7] using both flash evaporation and separate molecular beams of the components. Recently, a vapor phase deposition method was investigated[8]. Also, Nowak et al.[9] reported on a variation of the previously-mentioned closed-spacing vapor phase technique. None of these methods has led to the development of high quality device grade epitaxially grown layers of HgCdTe.

In our work, an open-tube horizontal slider-type technique[1] was selected as the basic liquid phase epitaxial growth scheme for the preparation of HgCdTe layers on CdTe or CdTeSe substrates. Thus, the upper limit for the mercury pressure in the system was about one atm. Although the LPE growth of HgCdTe from both a Hg solution and a Te-rich HgCdTe solution was considered, the Hg solution growth was not pursued because of possible problems with low melt temperatures ($<360°C$). For the Te-rich HgCdTe case, good quality LPE HgCdTe layers have been grown on both CdTeSe and CdTe substrates using a conventional horizontal slider system particularly adapted for solutions containing volatile Hg. The objectives of our HgCdTe epitaxial growth program are listed below:

1. Growth of layers with a high degree of alloy composition, carrier concentration and lifetime homogeneity.

2. Epitaxial layers with mirror-like surface morphologies which are suitable for photolithographic techniques.

3. Growth of alloy compositions over the entire range of x from 0.0 to 1.0.

4. Compositionally abrupt heterojunctions.

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5. Films with reproducible and controllable thicknesses and carrier concentrations.

6. Growth of multiple epilayers.

7. Theoretically abrupt optical transmission versus wave length curves.

8. 10^{14} cm^{-3} carrier concentrations.

9. High carrier mobilities.

10. High carrier lifetimes.

11. Uniform growth on large area substrates.

Although considerable progress has been made toward attaining some of the above objectives, much work remains to be done. Multiple layer growth and lifetime studies have not been initiated. The bulk of the research has been done on high-x material (arbitrarily defined as x values of $Hg_{1-x}Cd_xTe$ above 0.4, which is of interest for avalanche photodiodes). For this range of x, mirror-like layers, which exhibit a high degree of alloy homogeneity and with compositionally abrupt heterojunctions, have been grown. Thickness control was demonstrated by varying the growth time.

There is a need for high-quality epitaxial layers for low-x material (arbitrarily defined as x values of HgCdTe at 0.3 and below). For this range of x, LPE growth by our technique appears more difficult than for high x and only mediocre quality layers have been prepared.

II. PROGRESS DURING PROGRAM

A. LIQUIDUS ISOTHERMS

In order to use the liquid phase epitaxial technique, data on the phase diagram is required. Liquidus isotherms in the Te-corner of the HgCdTe phase diagram were determined by differential thermal analysis. A schematic of the DTA apparatus is shown in Fig. 1. Each sample was prepared by placing the required amounts of Hg, Cd and Te totaling 70 g in an evacuated, sealed, quartz ampoule. The sample along with a reference ampoule containing Si were placed inside a resistance furnace. Ceramic fiber was packed below and above the ampoules to ensure an isothermal temperature zone for the ampoules, which were heated to 650°C. Temperatures were measured with Platinel thermocouples. After homogenization of the melt, the furnace was cooled at a rate of 0.75°C/min until a thermal effect had been observed from the amplified differential signal. Corrections were made for supercooling effects by extrapolating measured temperatures to the zero degree super-cooling temperature. The reliability of the procedure was checked by deter-mining the melting points of pure Zn and pure Te in the same apparatus and with the same procedure. The measured values agreed within 1°C with the literature values of 419.5°C for Zn and 449.5°C for Te. The results of the DTA measurements are given in Table I. The temperatures for the formation of the first solid to freeze when cooling various liquid solutions of HgCdTe are given for the various compositions studied. The results for HgTe are in good agreement with the 1965 HgTe phase diagram of Strauss and Brebrick[10].

In Fig. 2, the liquidus sections of the temperature-composition phase diagram for the Te-rich portion of the HgCdTe systems are shown for x=0.0 to x=0.2. The data points are from Table I and the higher temperature values

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CERAMIC FIBER

PLATINEL
THERMOCOUPLES

FURNACE

SEALED RE-ENTRANT
EVACUATED QUARTZ
TUBES

TEST TUBE-SHAPED
QUARTZ AMPOULE

Si

LIQUID HgCdTe
(~ 70 gm)

CERAMIC FIBER

20 cm
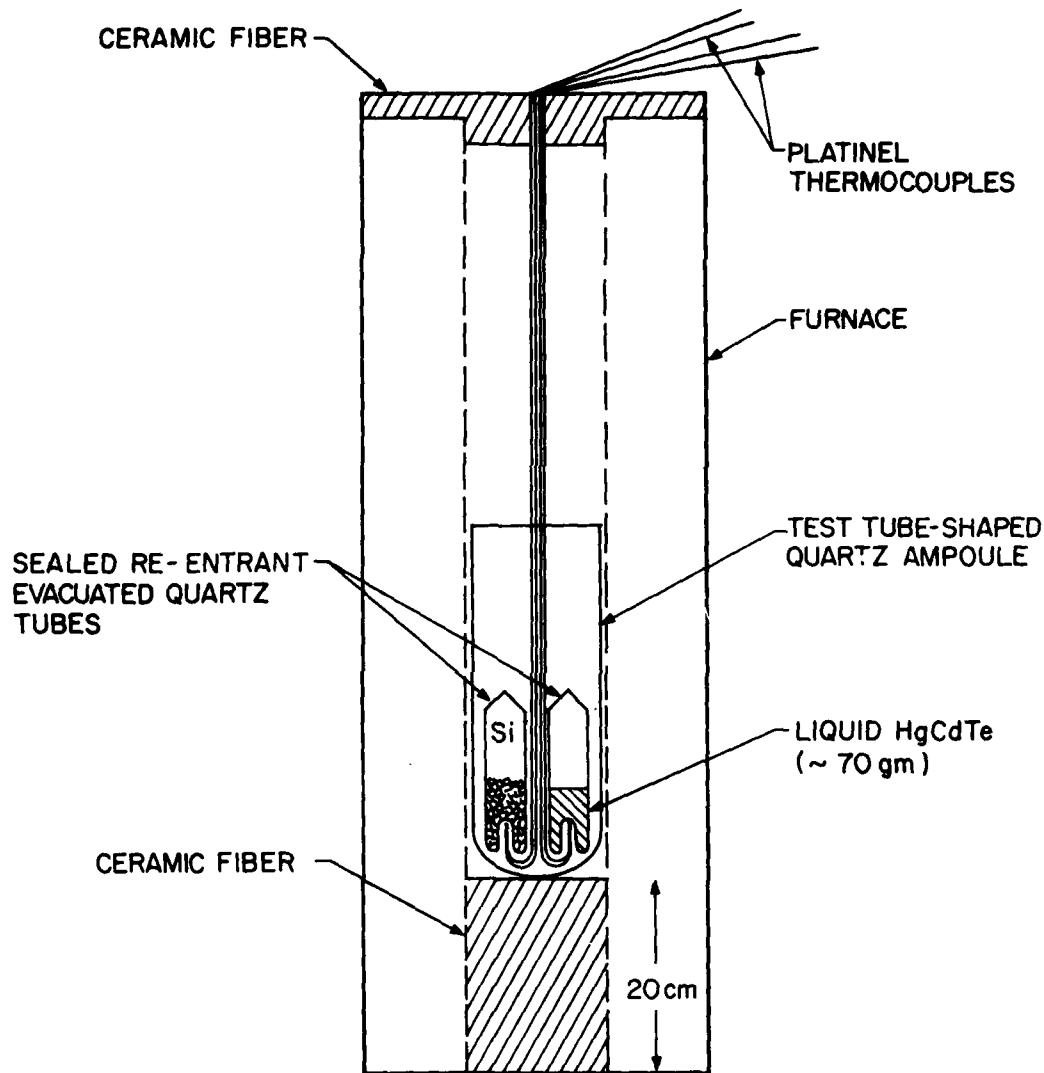
Fig. 1. A schematic of the differential thermal analysis (DTA)
apparatus used to measure liquidus temperatures of the Te-rich
HgCdTe phase diagram.

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TABLE I

TEMPERATURE FOR THE FORMATION OF THE FIRST
SOLID TO FREEZE WHEN COOLING LIQUID SOLUTIONS
OF $(Hg_{1-x_L}Cd_{x_L})_{1-y_L}Te_{y_L}$ (from DTA Data)

x_L, Cd	y_L, Te	T, °C
0	0.70	544
0	0.74	509
0	0.78	473
0	0.80	452.5
0	0.83	423
0.05	0.76	526
0.05	0.79	501.5
0.05	0.82	475.5
0.05	0.85	442
0.10	0.78	542.5
0.10	0.80	522.5
0.10	0.84	494
0.10	0.88	447
0.15	0.82	542.5
0.15	0.86	504
0.15	0.90	462
0.15	0.91	446.5
0.20	0.85	542
0.20	0.90	492
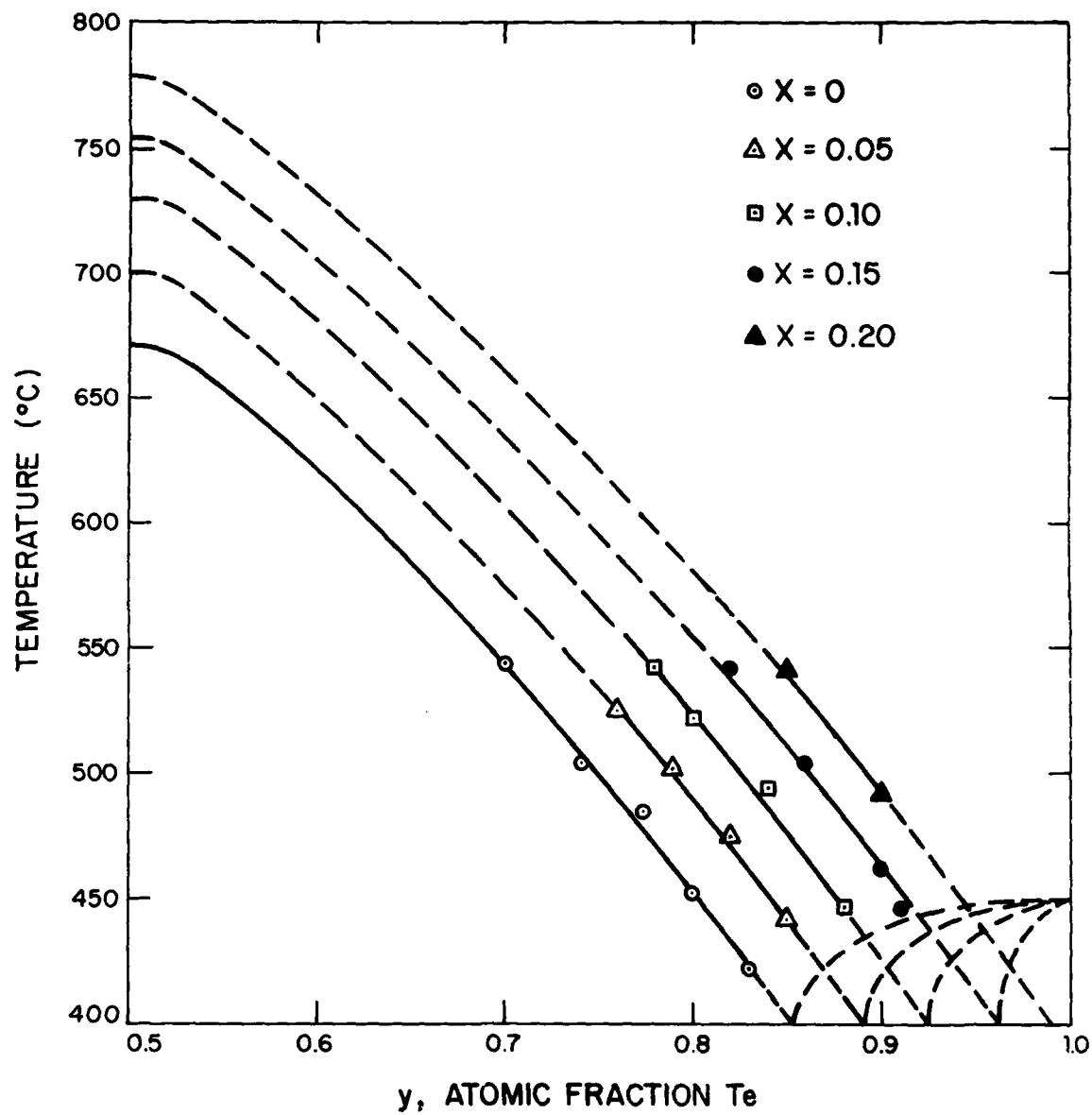
Fig. 2. Partial phase diagram of $(Hg_{1-x}Cd_x)_{1-y}Te_y$.

are interpolations using Laugier's[11] calculated values for high CdTe content alloys as a guide. The y=0.5 points are taken from the liquidus curve for the HgCdTe pseudobinary[12]. The DTA data for the region between the eutectic and pure Te temperatures are not shown.

In Fig. 3, liquidus isotherms in the 425-600°C temperature range for the Te-corner of the HgCdTe system are shown. The curves relate the atomic fraction of Hg, Cd and Te in the liquid state to the temperature and were obtained from the curves of the previous figure. It is seen that the solubility of Cd increases as the temperature is raised. Also, the solubility of Cd has a maximum with respect to the atomic fraction of Hg for constant temperature conditions. The dashed solidus isotherms are discussed in the next section.

B. LPE GROWTH AND SOLIDUS ISOTHERMS

For the first time in the HgTe-CdTe alloy system, liquid-phase epitaxially-grown layers have been prepared using an open-tube horizontal slider technique[1]. The LPE layers are grown from Te-rich HgCdTe solution in a H_2 flow and with less than 1 atm partial pressure of Hg over the melt. Growth temperatures were in the 450-550°C range and growth times varied from 15 sec to 10 min. The typical melt equilibration conditions are 1 h at 550°C. The degrees of rapid cooling prior to growth have been varied from about 0 to 100°C with typical values of 10°C for (111)A and 25°C for the (111)B orientations, respectively. Good layers have been produced primarily by equilibrating the solution melt with a source wafer of CdTe or CdTeSe prior to growth. The highest quality layers have been grown on (111) oriented substrates. Precision lattice matching does not contribute to improved layer quality at this stage of development of the growth technique.

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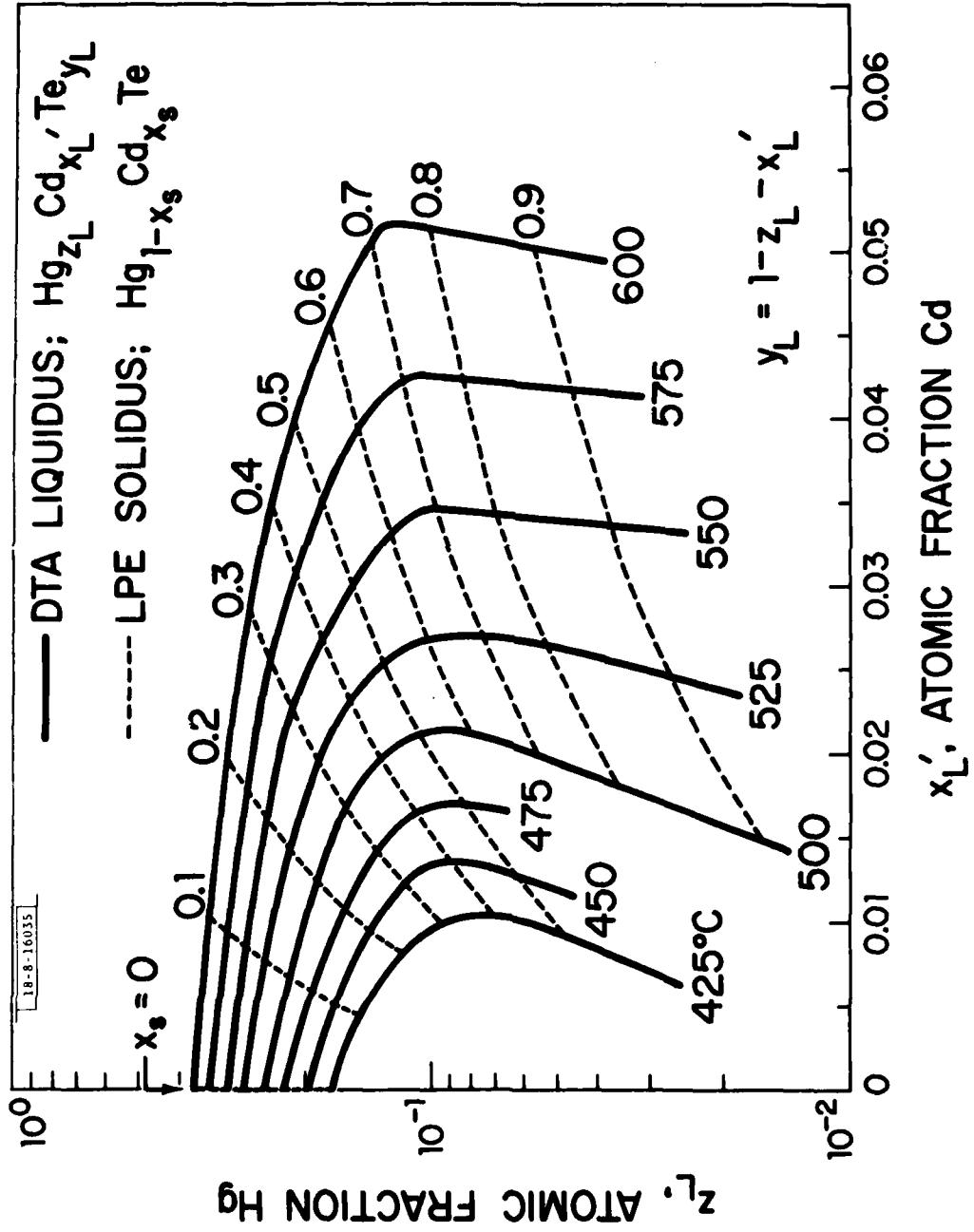
Fig. 3. Liquidus and solidus isotherms in the 425-600°C temperature range for the Te-corner of the HgCdTe ternary phase diagram.

In Fig. 4, a schematic diagram is shown of a section of the apparatus used for the open-tube liquid-phase epitaxial growth. The graphite barrel consists of a growth solution bin or reservoir, a slider, 4 x 10 mm inserts for the CdTeSe source wafer and (111)B or (111)A substrate. Approximately 1.5 g of source melt was placed in the 9 mm diameter solution bin. During a growth run, H_2 from a commercial Pd-diffused purifier is passed through the quartz tube and out through an oil bubbler. In order to achieve a solution composition which does not undergo excessive compositional changes with respect to time, an externally generated Hg vapor pressure is established over the growth solution throughout the experiments.

In Fig. 5, a schematic diagram of the temperature-time profile used for the LPE experiments is shown. The heat up time is about 10 min. The melt equilibrium time is typically 60 min to ensure adequate homogenization of all constituents. Generally, the furnace is allowed to cool without input power during the supercooling, growth and cooldown. During the growth part of the cycle, temperatures are lowered, usually 1.0-15°C, depending on the growth parameters and the layer thickness desired.

In Fig. 6, a schematic diagram of the HgCdTe and Hg-Te phase diagram are shown along with ten operational steps for LPE growth. Initially, the elements are weighed out for preparation of a quenched ingot, which yields the material used for the solution bin. The evacuated, sealed quartz tube containing the elements is heated to 650°C in order to react and homogenize the Hg, Cd and Te. The quartz ampoule is water quenched to room temperature. The source seed is inserted under the melt and equilibrated for typically 1 h. The

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EXTERNALLY GENERATED
Hg OVERPRESSURE

CONVENTIONAL HORIZONTAL
GRAPHITE SLIDER

H_2 →

H_2 →

CdTeSe
SOURCE
WAFER

SUBSTRATE
(III)B CdTeSe

GROWTH SOLUTION
IN THIS BIN

OPEN-ENDED
QUARTZ TUBE
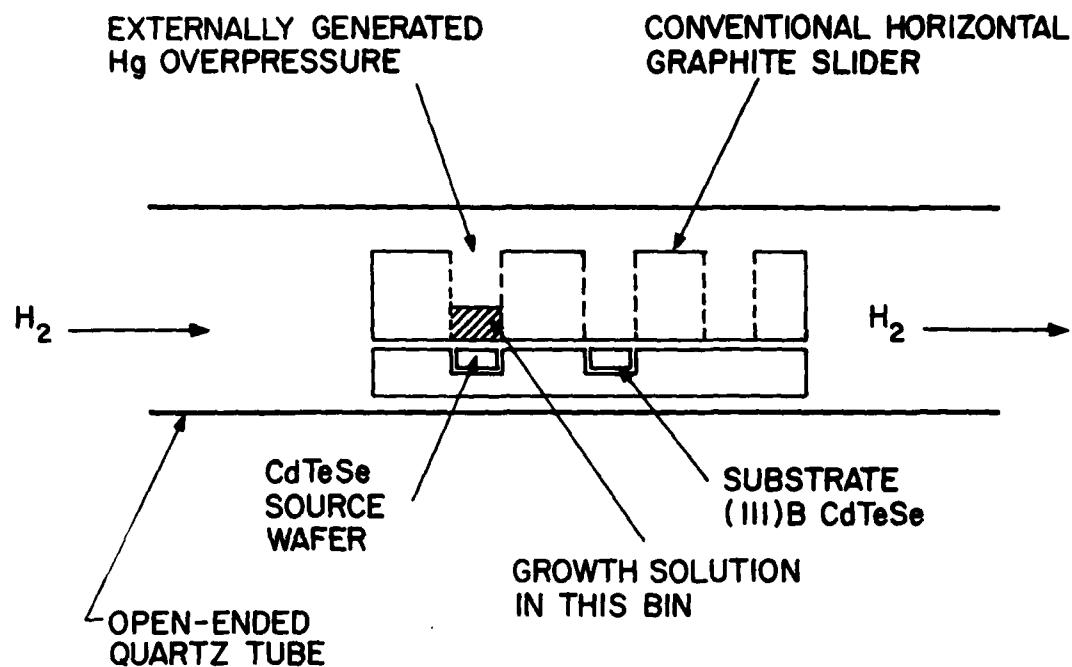
Fig. 4. Schematic diagram of a section of the apparatus used
for the open-tube liquid-phase epitaxial growth of HgCdTe lay-
ers on CdTeSe substrates.
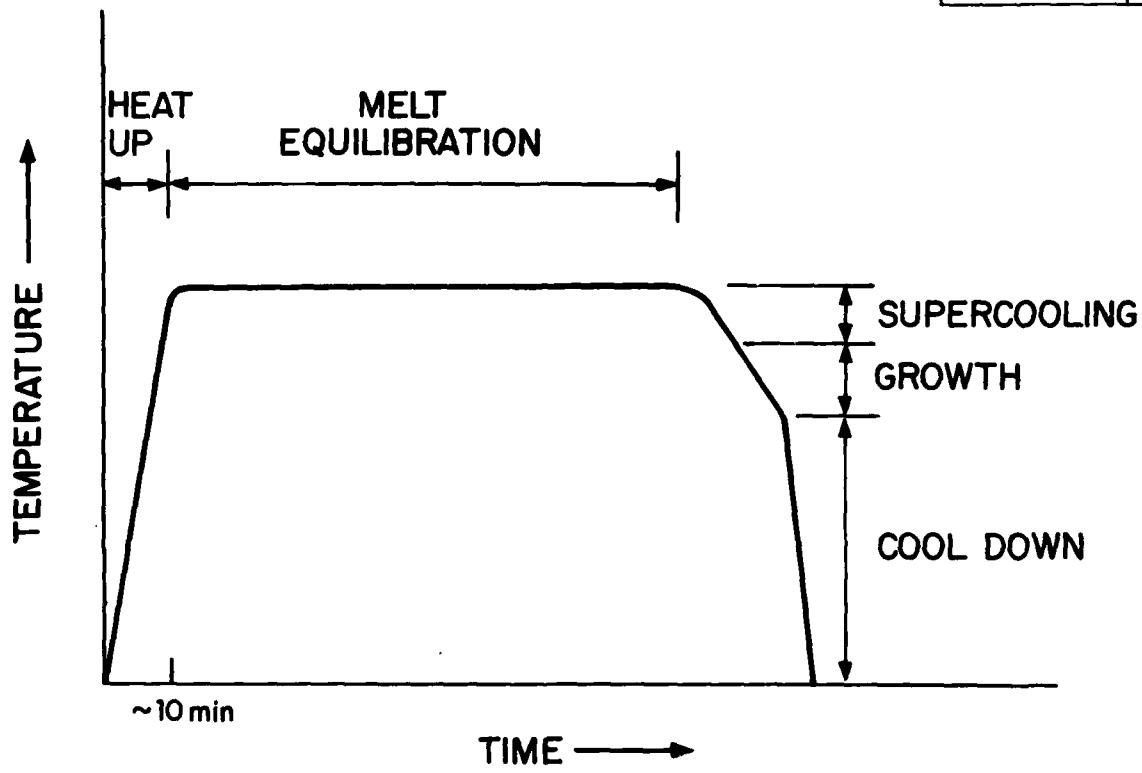
Fig. 5. Schematic diagram of temperature-time profile
of LPE experiments.

ATOMIC PERCENT TELLURIUM
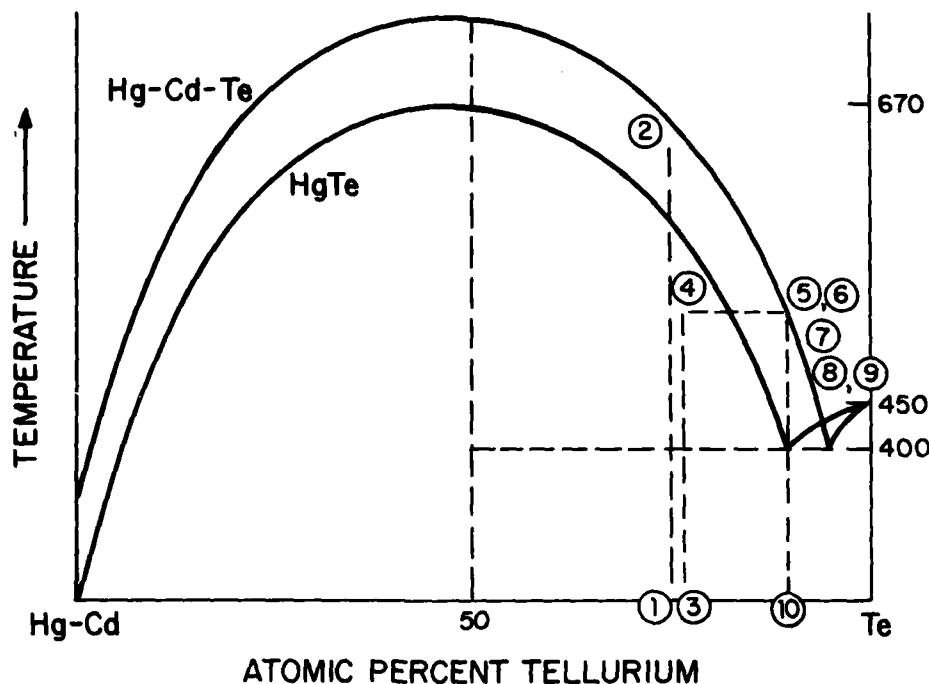
(1) WEIGH ELEMENTS FOR QUENCHED INGOT

(2) REACT AND HOMOGENIZE ELEMENTS AT 650° C

(3) WATER QUENCH $(Hg_{1-x}Cd_x)_{1-y}Te_y$ INGOT TO 300 K

(4) HEAT LPE SLIDER TO EQUILIBRIUM TEMPERATURE

(5) SLIDE SOURCE SEED UNDER MELT AND EQUILIBRIATE

(6) SLIDE SOURCE SEED OUT FROM UNDER MELT

(7) COOL TO THE GROWTH TEMPERATURE AND SLIDE
       SUBSTRATE UNDER MELT

(8) CONTINUE TO COOL TO GROW LAYER

(9) SLIDE SUBSTRATE OUT FROM UNDER MELT

(10) RAPIDLY COOL TO 300 K

Fig. 6. Schematic diagram of the HgCdTe and Hg-Te phase
diagram along with ten operational steps for LPE growth.

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source seed is removed from under the melt and the melt is supercooled. The substrate is inserted under the melt and a layer from 3 to 15 μm thick is grown, depending on the growth time. The substrate is removed from under the melt and rapidly cooled to room temperature.

In Fig. 7, the relationship between the liquidus composition and the solidus composition is displayed. The mole fraction of CdTe in the LPE-grown HgCdTe versus the ratio of the atomic fraction Hg to Cd in the liquid state is shown. The experimental solidus compositions were determined from electron microprobe measurements on the layers. The experimental liquidus compositions used for the data points were from the starting composition for the quenched ingots, which are used for the solution bin source material. In the LPE experiments, the Hg overpressure was adjusted so that an insignificant change in composition in the solution bin is believed to have occurred during heat-up, equilibration, supercooling, growth and cooldown. The experimental data are in reasonably good agreement with the pseudobinary tie-line data. This observation is consistent with the experimental result that the tie-line appears to be insensitive to the growth temperature. These correlations indicate that the Te-rich HgCdTe liquid solutions behave as nearly ideal solutions.

In Fig. 3, solidus lines denoted by the dashed curves are shown for various mole fractions of CdTe from 0 to 0.9. These curves relate the layer composition to the LPE growth temperature and the growth solution composition. It is seen that a very wide range of alloy compositions can be grown in the convenient temperature range of 425-550°C. These solidus isotherms were obtained by using liquidus curves of Fig. 3 and the tie line curve of Fig. 7.

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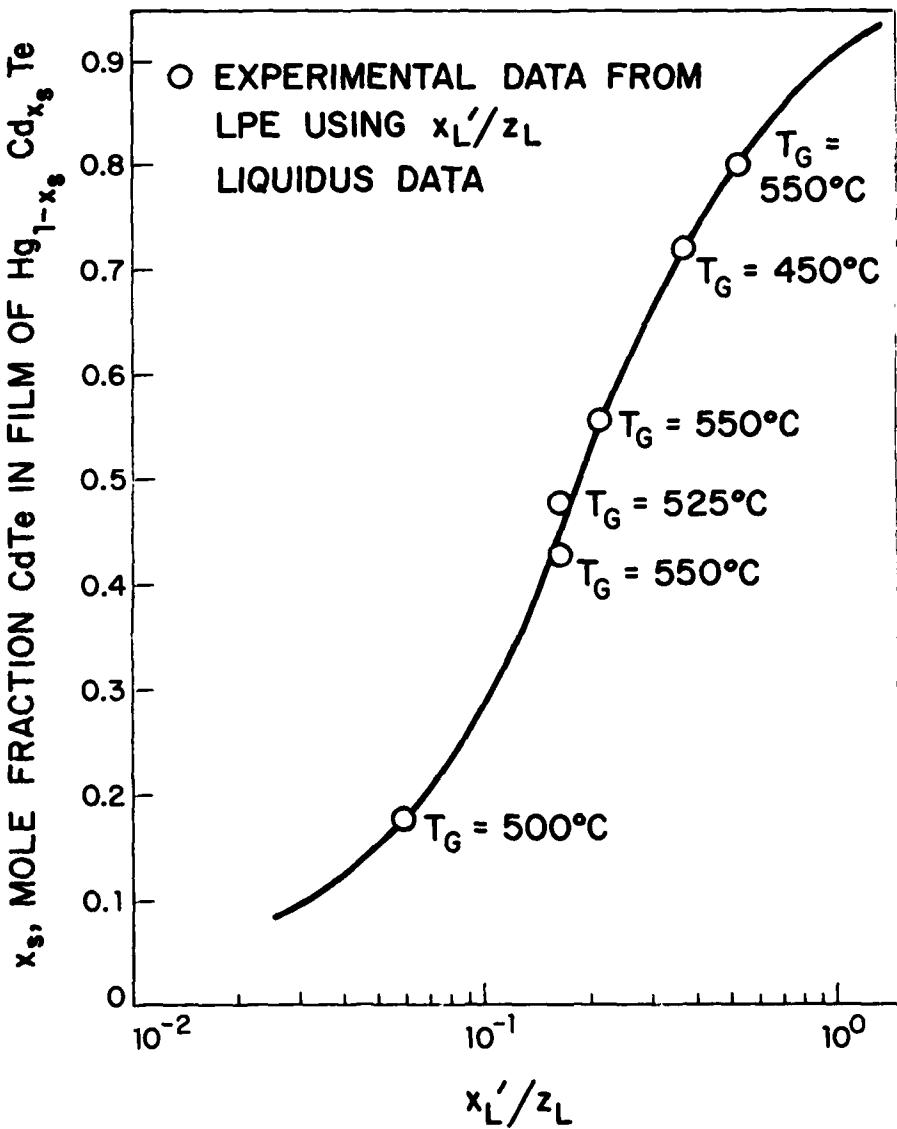
Fig. 7. The mole fraction of CdTe in the LPE-grown HgCdTe layer versus the ratio of the atomic fraction Hg to Cd in the liquid state.

C. CHARACTERIZATION OF THE LPE LAYERS

The LPE growth experiments and resultant layers have been characterized by several techniques such as optical microscopy, optical transmission and electrical measurements. Optical microscopy is used to observe the surface morphology and measure the layer thickness on a cleaved cross section of the layer-substrate composite. The magnitude and abruptness of the optical transmission is an indicator of layer quality. The optical cutoff wavelength correlates with alloy composition. Optically pumped laser, x-ray diffraction and some optical microscopy results for these layers were discussed in a recently published paper[1]. Only a few Hall coefficient and electrical resistivity measurements have been carried out, but the results indicate carrier mobilities and concentrations comparable to bulk materials.

The depth homogeneity of several LPE layers is given in Fig. 8. These data show that the depth homogeneity is very good. The lateral homogeneity is also very good as shown in Ref. 1. A composition profile in the direction perpendicular to the surface was obtained by making an electron microscope scan across a (110) face cleaved normal to the surface. The width of the graded region appears to be in the 3 to 5 μm range, but the spot size of the microprobe is about 3 μm, so that the actual width of the graded region is probably no more than 2 μm. The relatively abrupt single heterojunctions are probably a result of the short growth times and rapid cool-downs to room temperature after growth.

For each epitaxial layer, optical transmission measurements were made on the layer-substrate composite. In Fig. 9, the percent transmission in the vicinity of the absorption edge is plotted against both photon energy and wavelength for several representative layers. The area of the light spot in

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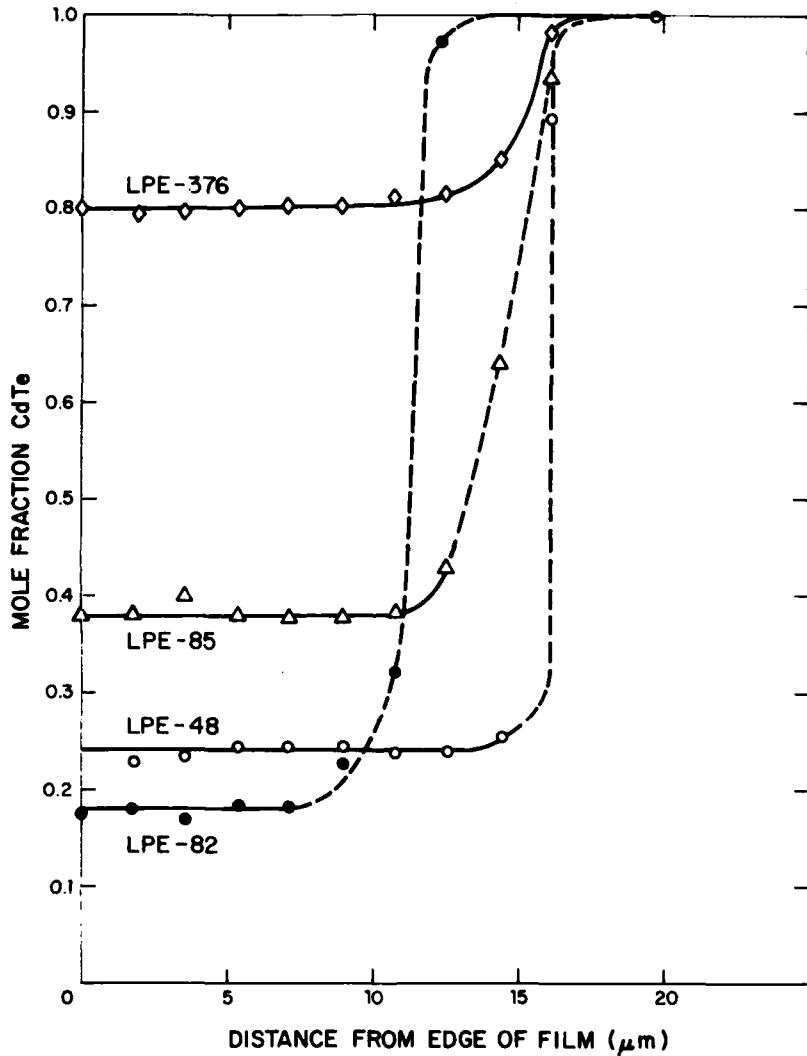
Fig. 8. Mole fraction CdTe as a function of distance from the edge of LPE-grown $Hg_{1-x}Cd_xTe$ layers on CdTeSe substrates.
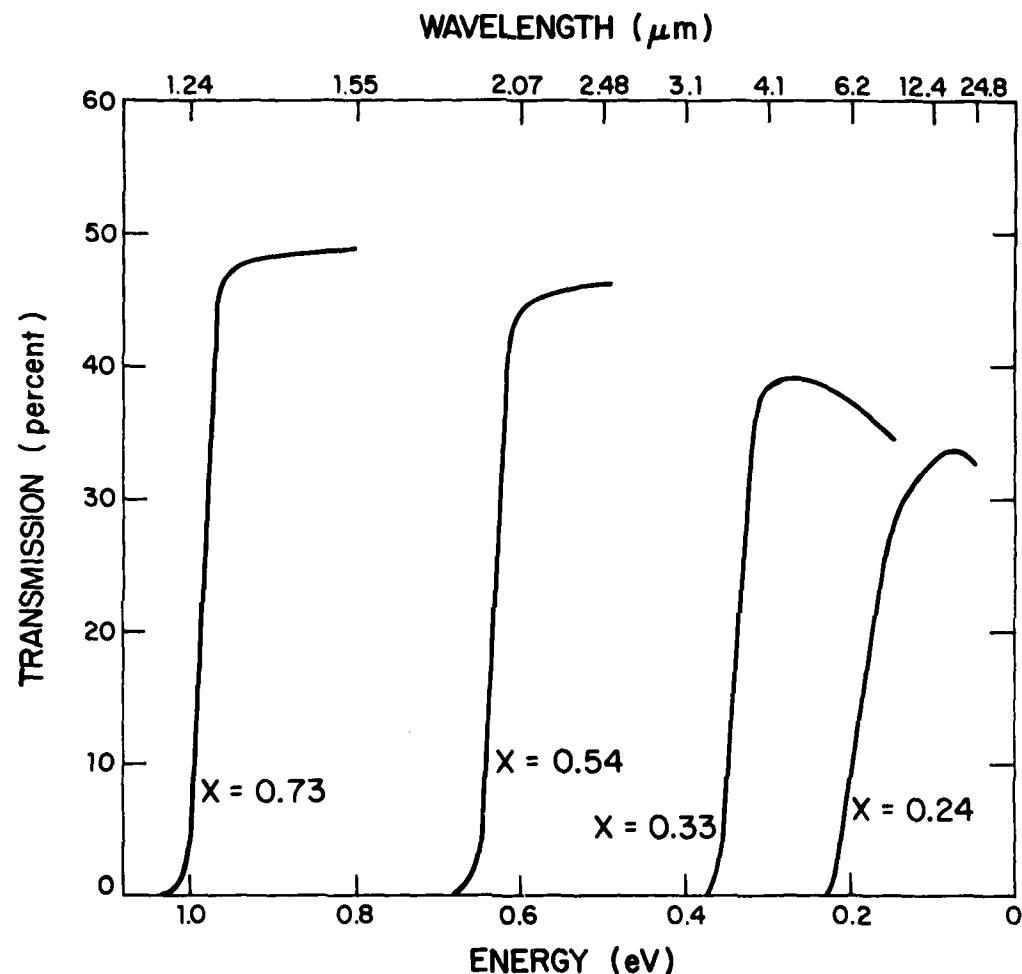
Fig. 9. Percent transmission in the vicinity of the absorption edge versus photon energy and wave-length for several representative substrate-$Hg_{1-x}Cd_xTe$ layer composites.

the double-beam spectrophotometer was about 25 mm^2. The mole fractions of CdTe in the HgCdTe layers were 0.73, 0.54, 0.33 and 0.24. The photon energies at half-maximum transmission are in reasonable agreement with the energy gaps.

Some electrical properties of as-grown and annealed LPE HgCdTe layers are shown in Table II. The nearly HgTe sample shows n-type behavior at both room temperature and 77K due to intrinsic carriers. The effective carrier mobilities or $R\sigma$ values are due to mixed conduction, since for this composition HgCdTe is a semimetal. For alloys with the higher CdTe content, the samples are p-type due to Hg vacancies. The electrical properties of layers annealed in Hg vapor are n-type. The carrier concentrations and carrier mobilities of as-grown and annealed LPE HgCdTe have a behavior which is comparable to bulk materials.

III. SUMMARY

Although the work is at a relatively early stage of development, the information obtained is summarized as follows:

1. High-quality $Hg_{1-x}Cd_xTe$ layers for high x on CdTeSe substrates have been grown from Te-rich solutions by LPE in an open-tube horizontal slider apparatus.

2. HgCdTe optical transmission and electron microprobe data indicate a high degree of alloy homogeneity.

3. Evidence for the growth of relatively abrupt single heterostructures has been obtained.

4. The electrical properties of as-grown and annealed LPE-grown HgCdTe layers are comparable to those of bulk material.

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TABLE II

ELECTRICAL PROPERTIES OF SOME AS-GROWN $Hg_{1-x}Cd_xTe$ LAYERS

SOLIDUS COMPOSITION, X	CONC. (cm^{-3}) AT 300 K	MOBILITY $(cm^2/V\text{-sec})$ AT 300 K	CONC. (cm^{-3}) AT 77 K	MOBILITY $(cm^2/V\text{-sec})$ AT 77 K
0.01	6.6×10^{17} N	14,000 N	5.1×10^{17} N	7,500 N
0.24	–	–	3.2×10^{17} P	160 P
0.35	–	–	2.9×10^{17} P	80 P
0.44	1.8×10^{17} P	60 P	3.6×10^{16} P	160 P
0.47	1.6×10^{17} P	160 P	2.9×10^{16} P	–

ELECTRICAL PROPERTIES OF ANNEALED (at 250°C) HgCdTe LAYERS

SOLIDUS COMPOSITION, X	FILM THICKNESS (µm)	ANNEAL TIME (hrs)	CONC. (cm^{-3}) AT 77 K	MOBILITY $(cm^2/V\text{-sec})$ AT 77 K
0.11	23	72	7.4×10^{16} N	90,000 N
0.19	2	1	4.6×10^{16} N	51,000 N

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13. See review article of Ref. 10.

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This report covers in detail the mercury cadmium telluride research work carried out on avalanche photodiode development at Lincoln Laboratory for the period 1 August 1978 through 30 September 1979. The topics covered are the liquid phase epitaxial growth of HgCdTe, liquidus isotherm determination by differential thermal analysis, optical and electrical characterization of various epitaxially grown layers on CdTe and CdTeSe substrates.

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